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# TAXONOMY AND CHEMISTRY OF THE WHITE PINES<sup>1</sup>

# N. T. MIROV

## TAXONOMY

The white pines comprise the section Haploxylon of the genus Pinus. According to Shaw (21), there are nineteen species of white pines. These he assigns to two subsections, Cembra and Paracembra. His subsections are further divided into groups of which five represent the white pines proper, and a sixth group, Cembroides, which represents the pinyon pines. Some botanists regard the white pines proper as a distinct genus separate from the pinyon pines, while others separate the section Haploxylon into three genera (15, p. 11-13). Shaw's classification of Haploxylon is as follows:

SUBSECTION CEMBRA

SUBSECTION PARACEMERA

Group Cembrae

- P. koraiensis Sieb. & Zucc.
- P. cembra L.

P. albicaulis Engelm.

**Group** Flexiles

P. flexilis James

P. armandi Franch.

**Group** Strobi

- P. ayacahuite Ehr.
- P. lambertiana Dougl.
- P. parviflora Sieb. & Zucc.

P. peuce Grisebach

- P. excelsa Hook.
- P. monticola Dougl.
- P. strobus L.

Group Gerardianse P. gerardiana Wall. P. bungeana Zucc. Group Cembroides P. cembroides Zucc. P. pinceana Gord. P. nelsonii Shaw Group Balfourianae P. balfouriana Murr. P. aristata Engelm.

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In the present paper Shaw's interpretation of section Haploxylon is accepted, but twenty-six species are recognized instead of nineteen. The seven additional species result from the elevation to specific rank of several pines that Shaw regards as mere varieties or as synonyms. These additional species are: P. sibirica Mayr., P. pumila Regal, P. pentaphylla Mayr., P. reflexa Engelm., P. monophylla Torr. & Frem., P. edulis Endl., and P. parryana Engelm. In the present paper the relationships between these twenty-six species are discussed in the light of their turpentine chemistry.

Of the eleven Old World species of section Haploxylon, one occurs in western Europe (P. cembra) and one on the Balkan Peninsula (P. peuce). One (P. sibirica) is essentially a Siberian pine. One (P. pumila) occupies the northeastern part of Asia. The remaining seven occur in southeastern Asia. All but one of the fifteen New World species of Haploxylon are concentrated in the western part of North America. This one is P. strobus, the typical phase of which occurs in the eastern part of the continent while P. strobus var. chiapensis occurs in the tropical parts of southeastern Mexico (Veracruz, Puebla, Oaxaca, and Chiapas). Thus, most of the white pines occur in southeastern Asia and southwestern North America.

The taxonomy of the Old World pines appears to be relatively simple. An exception is the status of *P. sibirica* and *P. pumila* and perhaps also that of *P. pentaphylla*. On the contrary, the taxonomy of most of the New World white pines is rather confusing. For instance, Shaw's *Pinus cembroides* in our opinion consists of four species: *P. monophylla*, *P. edulis*, *P. parryana*, and *P. cembroides*. Apparently there has been a great deal of interbreeding among this group of pines. Another taxonomically ambiguous group is that which is commonly referred to as the Mexican white pine. In reality this group consists of typical *P. ayacahuite*, which, with its two varieties *brachyptera* Shaw and *veitchii* Shaw, grows as far south as Guatemala, and *P. reflexa*, which grows in Arizona, New Mexico, western Texas and has been reported from the states of Chihuahua, Durango, and Nuevo Leon of Mexico.

The author has had the opportunity of studying *P. reflexa* in the Apache Indian Reservation, Arizona. It grows there at an elevation of about 8,000 feet in association with ponderosa pine, Douglas fir, and white fir, with occasional aspen and New Mexican locust underneath. In that locality *P. reflexa* is a tall, straight forest tree which resembles *P. monticola* rather than *P. flexilis*, a "low, thick-trunked much branched tree" (24, p. 7). Sudworth says that "in exposed, higher situations *P. reflexa* has a general resemblance to the limber pine." The synonymy of *P. reflexa* is rather confusing; some botanists call it *P. strobiformis* Sudw. (25, p. 14), others refer to it as *P. ayacahuite* var. brachyptera (20, p. 11, pl. 6). According to Sudworth (24), Engelmann named a variant of *P. ayacahuite* as *P. flexilis* var. *reflexa* and four years later elevated it to the rank of species as *P. reflexa*, a name under which all Mexican white pines were long known to American botanists. In 1889 Sargent (16) pointed out that *P. reflexa* and *P. strobiformis* were synonyms. Little (7) adopts Engelmann's original classification of it, namely *P. flexilis* var. *reflexa*. Dr. Maximino Martinez, a profound student of the Mexican pines, is inclined to follow the later decision of Engelmann and call it *Pinus reflexa* (8), a decision in which we concur. In his "Los Pinos Mexicanos" (8, p. 117), Dr. Martinez displays in a diagram of the section *Ayacahuites*, his concept of the relations of this pine to other closely related white pines. Since *P. monticola* is not known from Mexico, it is not included in Martinez's diagram.

### CHEMISTRY

Erdtman (3) and his associates have shown that the section *Haploxylon* differs from the section *Diploxylon* in the composition of the heartwood phenols. Pines of the *Haploxylon* section are characterized by stilbenes and dibenzyls as well as flavones and flavanones derived from phloroglucinol; the group *Strobi*, in addition, contains flavones and flavanones derived from methylphloroglucinol. Monomethyl ether of inositol (pinite or pinitol) is present in all white pines (however, there is very little if any in *P. aristata*).

Pines of the section *Diploxylon* possess stilbenes but not corresponding dibenzyls; flavanones are present but flavones are not. Pinitol is absent. The two sections are thus clearly distinguishable from each other biochemically. Unfortunately a further subdivision based on the heartwood phenols is possible only in a few cases.

In the present paper the author endeavors to discuss the chemical composition of the turpentines of the white pines (Pinus, section *Haploxylon*). However, it must be pointed out that the chemical picture is not yet complete. There are still eight pines in which the turpentines have not been analyzed. Some of these pines (*P. armandi*, *P. bungeana*) are difficult of access, and it appears that their turpentines may remain unknown for some time.

It is not the author's intention to devise a chemical classification for pines that would replace the existing morphological classification. The purpose of this paper is merely to show that there are spheres of chemical relationship among different pines. This information along with other evidence may be used by botanists when the taxonomy of pines is revised.

Turpentine is the volatile part of oleoresin, or pitch, of pines and other conifers. It is not a pure chemical substance but a mixture of several chemical compounds, mostly terpenes  $(C_{10}H_{16})$ .

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A major component of all pine turpentines is alpha-pinene. In the section *Haploxylon* only *P. albicaulis* lacks this turpene (6); all other white pines possess varying amounts of alphapinene, in some species up to 98 percent of the total amount of turpentine. Other terpenes—beta-pinene, limonene, delta-3carene, terpinolene—occur in some white pines in smaller quantities. Sesquiterpenes ( $C_{15}H_{24}$ ) occupy a subordinate position; these are important in determining chemical relationships of the pines. Oxygen-containing terpene derivatives are rare and probably often of a secondary origin (oxidation during collecting, storing, and distilling the oleoresin).

Very interesting is the occurrence of saturated straight chain hydrocarbons, heptane ( $C_7H_{16}$ ) and undecane ( $C_{11}H_{24}$ ), in several white pines. These hydrocarbons are found also in some *Diploxylon* pines: ninety-five percent of turpentines of *P*. *Jeffreyi* and *P*. *sabiniana* consists of n-heptane.

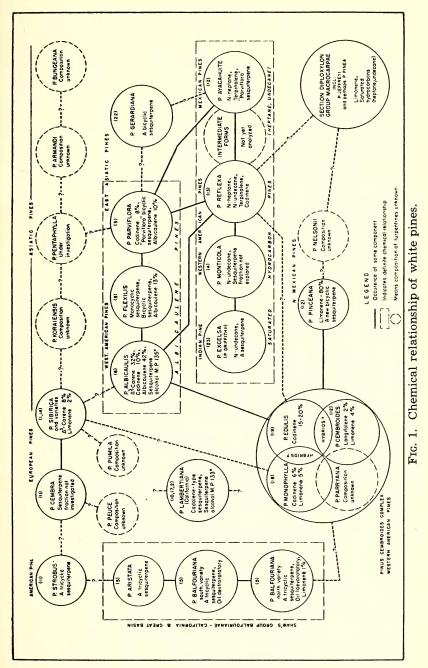
All *Haploxylon* pines and the chemistry of the turpentines of most of them are represented diagramatically in fig. 1. Solid line circles denote those pines whose turpentines have been investigated; broken line circles represent the pines that have not yet been investigated. Rectangular boxes indicate groups of pines possessing a similarity of chemical composition of their turpentines. Solid lines indicate chemical relationship between different pines. Broken lines suggest a possible relationship. Numbers in parentheses refer to the literature references listed at the end of the article.

In considering the turpentine chemistry of the white pines, we should keep in mind that the present composition of the section *Haploxylon* is probably very different from the composition of its progenitors in previous geological periods. Pines probably originated during the Permian period, and the *Haploxylon* pines were separated from the *Diploxylon* pines very early in history, perhaps during the Jurassic. No living species of pine occur in deposits older than those of Miocene (9), so we may assume that many connecting links between different pines have been lost in the past. For instance, the presence of saturated hydrocarbons in some pines is probably of a very ancient origin, and it is possible that in the past geological periods there were more pines containing saturated hydrocarbons than now (23). Most such pines apparently disappeared long ago.

Saturated carbons, which rarely occur in contemporary pines, are found in the following four species of the group *Strobi*: *P. excelsa*, *P. monticola*, *P. reflexa*, and *P. ayacahuite*. Undecane was discovered in *P. excelsa* of India by Simonsen and Rau (23). Later this hydrocarbon was found in *P. monticola* (4) and in some hard pines. *Pinus reflexa* (13) contains two saturated hydrocarbons, undecane and heptane, and a sesqui-



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terpene—cadinene. The fourth species of this chemical group, *P. ayacahuite*, possesses heptane but no undecane (21).

A bicyclic sesquiterpene occurring in *P. ayacahuite* is apparently identical with the sesquiterpene of *P. parviflora*. The presence of a bicyclic sesquiterpene in *P. gerardiana* (22) of Kashmir and Afghanistan suggests a chemical relationship of this pine to *P. ayacahuite* on one hand and to *P. parviflora* on the other.

The presence of n-undecane in *P. lambertiana*, reported by Schorger (17), has not been substantiated by more recent studies (10). This pine is difficult to cross with other white pines and it stands alone in chemical composition of turpentine. It is an endemic pine of California and Oregon, but apparently, judging by the physical constants of its turpentine, it possesses a considerable variability (2), and should be studied more intensively. It might be possible that its sesquiterpene alcohol (melting point 133° C.) is identical with the sesquiterpene alcohol of *P. albicaulis*.

Pinus albicaulis occupies a unique position among the white pines. Morphologically it is grouped with P. cembra, P. sibirica, P. pumila, and P. koraiensis. The chemistry of its turpentine is the most complicated of all white pines linking it not to those species with which it is morphologically related, but to others. Pinus albicaulis turpentine contains a diterpene, and appreciable amounts of a sesquiterpene, albicaulene (6), the latter being found also in the turpentines of P. flexilis and P. parviflora (5). On the other hand its turpentine contains a sweetsmelling terpene, delta-3-carene, which is also found in P. sibirica, but is rare in other white pines. The presence of a sesquiterpene, cadinene, in P. albicaulis turpentine suggests a relationship of this pine with the P. cembroides complex.

Pinus cembra (11) and related Eurasian pines shown on the top of the chart (fig. 1) have not been adequately studied. Nevertheless, it is evident that P. cembra, an alpine species of western Europe, is chemically different from the Eurasian P. sibirica. The latter pine, occupying an extensive area from Kola peninsula in northwestern Russia to beyond Lake Baikal in eastern Siberia, possesses several morphologically different varieties (such as P. coronans Litw.) as well as chemically different varieties (14, 1). Pinus pentaphylla is now under investigation, but the two extremely interesting southeastern Asiatic species, P. armandi and P. bungeana, still remain unknown. It is to be expected that their turpentines are rather complicated.

*Pinus aristata* and *P. balfouriana* belong, according to Shaw (21) to group *Balfourianae*, the foxtail pines. This group is represented on the left side of the chart (fig. 1). Chemically as well as morphologically these two pines have a great deal in common. The harmonious picture is slightly complicated by

our finding that P. balfouriana from northern California is somewhat different from the disjunct population in the southern Sierra Nevada. The northern locality is west of Mount Shasta; the southern locality is not far from Mount Whitney. The two localities are separated (and probably have been since before the Pleistocene) by a distance of 400 miles. We have studied turpentines from the two localities (5) and have found that both of them contain a tricyclic sesquiterpene, but that the turpentine from the northern location contained some betapinene and limonene, while that from the southern location lacked these components but contained some bornyl acetate. Both turpentines consist mainly of alpha-pinene, but in the northern location there was predominance of a laevorotatory antipode of this terpene while in the southern location, a dextrorotatory antipode prevailed. Pinus balfouriana is a pine of alpine environment and its two populations, the northern and the southern, have not been compared closely by botanists. It is generally assumed, however, that pines from the two localities are morphologically identical.

Although there is a very close relationship between the two populations of *P. balfouriana*, the chemical composition of their turpentines indicates that there are noticeable and important differences perhaps not yet perceptable to the human eye, but easily detectable by the precise laboratory instruments. Since the geographic separation of the two populations, some changes have taken place which now distinguish them. We are witnessing here, perhaps, a step in the origin of a new species.

Pinus aristata (5) is closely related chemically to both forms of P. balfouriana. It is not certain if the tricyclic sesquiterpene of P. aristata is the same as the tricyclic sesquiterpene of P. strobus. Nevertheless, it is significant that the latter pine also possesses a tricyclic sesquiterpene.

Of the four pines constituting the *P. cembroides* complex, one species, *P. parryana*, has not yet been investigated. *Pinus* monophylla has cadinene and limonene in its turpentine, the latter a terpene relatively rare in white pines. Cadinene is also found in *P. edulis*, but no limonene. While the percentage of cadinene in typical *P. monophylla* of western Nevada is rather small (6 per cent), it apparently increases eastward, and in Utah, where *P. monophylla* apparently crosses with *P. edulis*, cadinene may reach fifteen percent of the total weight of turpentine.

*Pinus cembroides* has no cadinene but another (tricyclic) sesquiterpene, longifolene, which occurs in some hard pines (*P.torreyana* of the group *Macrocarpae*, and *P.roxburghii* of the group *Longifoliae*) and in some other Asiatic pines. Limonene also occurs in *P. cembroides*, indicating a closer affinity between *P. cembroides* and *P. monophylla* than between *P. cembroides* and *P. edulis*. In *P. pinceana* a new (bicyclic) sesquiterpene appears. This pine belongs along with the *P. cembroides* complex to the group Cembroides, the desert nut pines of southwestern North America. Pinus pinceana turpentine is outstanding in being composed mostly of limonene. The chemistry of the turpentine of P. Nelsonii is not yet known. It must have an interesting composition.

The chemical picture of the P. cembroides complex is thus very similar to the botanical picture as suggested by Martinez in his "Los Pinos Mexicanos" (8, p. 117), while the presence of large quantities of limonene in *P. pinceana* links the group Cembroides with the group Macrocarpae of Section Diploxylon. (Limonene in large quantities is also found in P. pinea, P. serotina and in P. lumholtzii.) On the other hand, the presence of the saturated hydrocarbons of the Macrocarpae pines suggest their relation to P. reflexa and other white pines containing these hydrocarbons.

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# A NEW SPECIES OF CLARKIA (ONAGRACEAE)

#### HARLAN LEWIS AND W. R. ERNST

Clarkia similis sp. nov. Herba erecta altitudine ad 9 dm.; caulibus simplicibus vel ramosis; foliis angusto-lanceolatis vel elliptis, denticulatis, 2–4 cm. longis, 3–8 mm. latis, in basi ad petiolos usque ad 8 mm. longo angustatis; inflorescentium axe in apice recurvato; calycis tubo 1.5-2 mm. longo, annulo pilorum ad apicem posito, limbo 6–10 mm. longo, circiter 1.5 mm. lato; petalis 6–12 mm. longis, 3–6 mm. latis, oblanceolatis vel rhomboideis vel obovatis subintegris, acutis vel rotundatis, in basi in unguiculum gracilis circiter 1 mm. longum angustatis, albis vel pallidis in parte inferior purpureo-punctulatis; staminibus 8, plerumque ab stigmate liberis; stigmate quadrifido, lobis brevibus; stylo aequante stamines; ovario 8-canaliculato, 1.5–2.5 cm. longo; capsula 1.5–3 cm. longa, 1–1.5 mm. lata.

Erect herb as much as 9 dm. tall; stems simple or branched, puberulent above with short upwardly curled hairs sometimes sparsely so, sparsely puberulent to glabrate below; leaf blades narrowly lanceolate to lanceolate-elliptic, subentire to denticulate, 2–4 cm. long, 3–8 mm. broad, the apex often obtuse, glabrate to sparsely puberulent, narrowed into petioles as much